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Photocatalytic Decomposition of Trypan Blue Over Nanocomposite Thin Films

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Abstract

The photocatalytic activity of titanium dioxide (TiO₂) and gold (Au) modified TiO₂ (Au/TiO₂), supported in polymethylmethacrylate (PMMA) thin film, was evaluated in the photodegradation of Trypan Blue (TB) under sunlight irradiation. The effect of parameters such as the photocatalyst amount and pH on TiO₂ photocatalytic activity is investigated. Oxygen flow stream was applied to enhance the decomposition process of TB. The maximum photoactivity was attained using Au/TiO₂-PMMA thin film at pH=2.

Keywords: TiO₂, Au/TiO₂, photocatalyst, Trypan Blue, PMMA & pH

1-Introduction

The existence of organic dyes in wastewaters has become a serious problem because of the synthetic nature of organic dyes [1]. Trypan blue is an azo dye that is reported as a carcinogenic agent [2]. It has a complex structure with a high photostability [3]. So there is a need for an efficient economic method for the degradation of such stable compounds.

The use of solar energy to drive the destruction of pollutants presents an indubitable advantage from the environmental viewpoint [4]. It also improves the economic achievability of the process, making it competitive with other technologies for wastewater management, such as ozone or H₂O₂/UV-C [5].

It has been reported that some semiconductor fine particles coated with polymer are excellent photocatalysts [6], due to their unique electronic and optical properties. This facilitates efficient photon-induced generation and the separation of charges that can be utilized for selective oxidation and reduction reactions at the semiconductor's surface [7].

TiO₂ is the most widely used catalyst, essentially because of its photostability, non-toxicity, low cost and water insolubility under most environmental circumstances [8]. Even though nanocrystalline TiO₂ has been shown to be an extremely active photocatalyst [9], this technology has not yet been successfully commercialized because of the problems linked to the separation of TiO₂ particles from the suspension after treatment. In order to solve this problem, supported photocatalysts have been developed [10–12]. Many research efforts have been focused on the holding of titania nanoparticles onto silica materials using different reactor configurations, such as silica gel particles slurries [13], glass electrodes [14], and fluidized beds [15]. TiO₂ supported on clinoptilolite

was used efficiently as a catalyst for photocatalytic degradation of azo dye Disperse Yellow 23 in water. This study shows that pH is one of the main affecting factors on the degradation of azo dye Disperse Yellow 23 [16]. TiO₂ codoped with Fe³⁺ and Ho³⁺ ions was more powerful in the photocatalytic degradation of methyl orange than TiO₂ alone. This was ascribed to the fact that some elements such as Fe³⁺ and Ho³⁺ broaden the absorption profile, generate more electron-hole pairs and retard the recombination of photo-generated electrons and holes [17].

The goal of this work is to develop a method for the immobilization and easy separation of the used nanoparticles (Au/TiO₂) by supporting them into PMMA thin film. PMMA was chosen because this type of plastic is UV transparent and easy mouldable [1]. Moreover, photocatalytic thin films can shatter down organic dirt, kill bacteria and destroy harmful molecules in water and air by using light as the energy source [18].

In this study, TiO₂ and surface modified TiO₂ with Au (Au/TiO₂) particles supported in PMMA thin film were used for the photocatalytic degradation of the azo dye TB (carcinogenic hazardous water contaminant) under irradiation with sunlight.

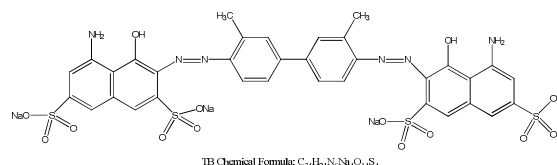


Figure 1: TB chemical structure

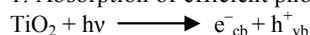
Photodegradation of organic compounds using a semiconductor catalyst takes place when the catalyst

is illuminated with light of energy ($h\nu$) more than or equal to the band gap energy. Electron/hole pairs are generated in the bulk. These charge carriers migrate towards the catalyst surface, where they take part in redox reactions with adsorbed organic molecules.

In this study, sunlight was used as an energy source for the excitation of catalyst electrons from filled valence band (vb) to empty conduction band (cb). The photocatalyst, in presence of sunlight and oxygen flow stream, decomposes the organic species to CO_2 and H_2O [19].

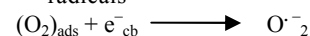
The most commonly proposed mechanism for the mineralization of most organic pollutants is the following [20-21]:

1. Absorption of efficient photons

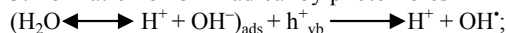


Where, h is the planks constant, ν is the light frequency, e^-_{cb} is the electron of conduction band and h^+_{vb} is the hole of valence band.

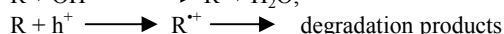
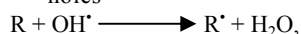
2. Oxygen adsorption (ads.) leading to $\text{O}^{\cdot -}_2$ free radicals



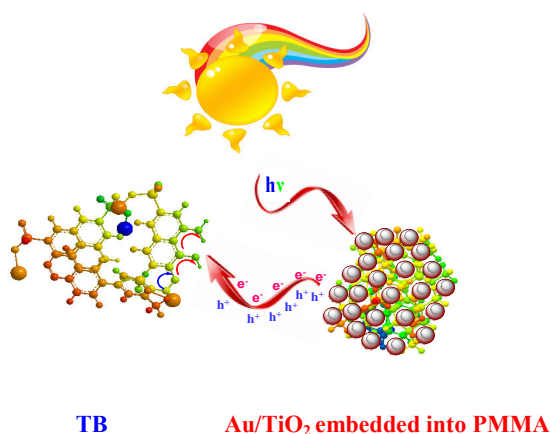
3. Formation of OH^{\cdot} radical by photo-holes



4. Oxidation of organic species (R) by OH^{\cdot} radical or holes



Scheme 1 illustrates the mechanism of TB photocatalytic degradation process using Au/TiO₂-PMMA thin film and sunlight irradiation.



Scheme 1: TB photocatalytic degradation process.

2-Experimental

Chemicals: The P25 TiO₂ (ca. 80% anatase, ca. 20% rutile) supplied by Degussa, with a typical surface area of $50 \pm 15 \text{ m}^2/\text{g}$, average primary particle size 21 nm and band gap 3.03 eV for rutile and 3.18 for anatase.

2.1. Preparation of Au/TiO₂

50 ml aqueous solution contains 0.08 g TiO₂ and 5 ml of $5 \times 10^{-3} \text{ mol dm}^{-3}$ HAuCl₄ (Aldrich) was stirred whilst heating until boiling. Then 1 ml of 0.5% of sodium

citrate, Puriss (Fluka) was added during heating until the colour changed. The deposition of gold nanoparticles on TiO₂ is confirmed by the colour change of the modified oxide powder, turning from white into deep purple, a colour deriving from the surface plasmon resonance of Au⁰ islands [22]. The solution was removed, centrifuged, washed 3 times with methanol and 6 times with water, and dried overnight at 90 °C.

2.2. Polymer synthesis

PMMA polymer was prepared according to the free radical polymerization process [23]. Methyl methacrylate (99.0%, Fluka) was purified via distillation under reduced pressure. About 100 ml (density 0.943 g/mL) of purified methyl methacrylate monomer was taken in a Pyrex glass jar. Traces of benzoyl peroxide were added to catalyze the radical polymerization. The mixture was deoxygenized by purging with argon. Oxygen may cause oxidative degradation of macromolecules that have already been formed [24]. The jar is then sealed and kept undisturbed for 48 h at 55 °C. The temperature is raised gradually to 90° C for 5 h to get rid of the remaining traces of unreacted initiator and monomer by evaporation [25]. Before taking the samples out of the oven, its temperature is decreased slowly to 25 °C over a period of 24 h.

2.3. Preparation of TiO₂ thin film:

First, 300 mg PMMA was dissolved in 10ml tetrahydrofuran (Fluka). A proportional amount of TiO₂ (0.04,0.08g) powder was suspended in the dissolved polymer. The mixture was uniformly distributed in a Pyrex glass Petri dish (100 mm in diameter) and left to dry for 24h at room temperature. Au/TiO₂ thin film was prepared by the same method.

2.4. Preparation of gold nanoparticles

gold nanoparticles was prepared by chemical reduction of HAuCl₄, according to Turkevich's method [26], 95 mL of a chlorauric acid (HAuCl₄) solution containing 2.5 mg of Au is refluxed and 5 mL of 1% sodium citrate solution is added to the boiling solution. The solution is further boiled for 30 min and is then left to cool to room temperature.

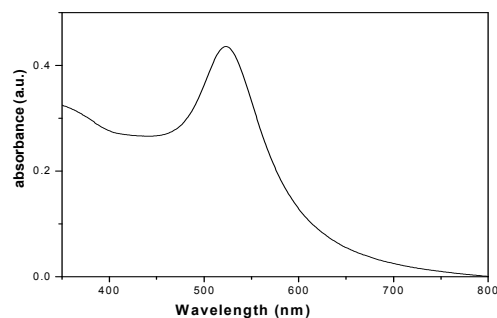


Figure 2: Absorption spectra of the synthesized gold (0.025 mg/ml) nanoparticles using optical path length of 1cm.

Figure (2) shows the absorption spectra of gold nanospheres. The spectrum of the gold nanospheres has an intense band at 521 nm assignable to the plasmon absorption of a 22 nm particle diameter of gold. [27,28].

2.5. Photocatalysis experiment:

The photocatalysis experiment was carried out by exposing 100 ml of the aqueous TB samples over the PMMA thin film in a Petri dish to outdoor sunlight. The dried PMMA thin film was maintained in the bottom of the Pyrex glass Petri dish (100 mm in diameter) by holding large lipped paper clips vertically across the dish boundary. The values of natural sunlight irradiance were measured on the Three Channel Eldonet Dosimeter (Germany), and the concentration of TB was $1 \times 10^{-5} \text{ mol dm}^{-3}$. Two control experiments were carried out: In the first, TB solution only was exposed to sunlight. In the second, TB solution over blank PMMA thin film (without nanoparticles) was exposed to sunlight. The effect of pH on the photodegradation of TB was investigated over the pH range of $2-8 \pm 0.1$ by addition of HCl and NaOH. The temperature was maintained at $22-25^\circ \text{C}$ by using an ice-water bath. Airing by oxygen was done in all experiments using a battery powered (3V) portable aquarium fish tank air pump (R-104). Samples (3ml) were taken out at regular time intervals for analysis using a Perkin Elemer λ_{40} spectrophotometer (USA). Data acquisition and manipulation were performed using UV-winlab λ_{40} and origin 7 computer based programs.

3-Results and Discussion

Effect of pHs:

TiO_2 -PMMA thin film was used to examine TB photostability in neutral, acidic and basic media. The pH of the sample is an important parameter in the photodegradation taking place on semiconductor particle surfaces, since it is related to the surface charge properties of the photocatalyst. The pH of an electrolyte can vary the surface charge of the photocatalyst and also shifts the potential of some redox reaction. Thus, it affects the adsorption of organic solutes [29]. On the other hand, TiO_2 surface charge is zero at pH 6.3. This means that the TiO_2 surface is positively charged (Ti-OH_2^+) when the pH is lower than this value and negatively charged (Ti-O^-) when the pH is higher than this value[30].

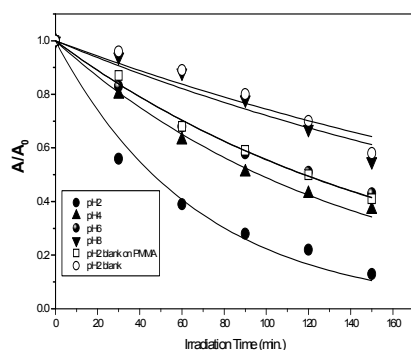


Figure 3: Effect of different pHs on TB ($1 \times 10^{-5} \text{ mol dm}^{-3}$, $\lambda_{\text{max}}=585\text{nm}$) degradation efficiency using 0.08 g TiO_2 -PMMA thin film and sunlight irradiance $500-600 \text{ W/m}^2$.

With raising the pH value the rate of photodegradation, efficiency decreases (Fig. 3). Shifting the pH from highly acidic pH2 towards pH6 decreases the photodegradation rate due to decreasing the positive charge at the surface. As a result, the adsorption and electron injection on the surface will decrease. At $\text{pH} > 6.3$ TiOH and TiO^- species are present as found by Herrmann and his co-workers [34]. TB and TiO_2 surface existed under negative forms. Therefore, repulsions are much more marked because both species are negatively charged, thus preventing interactions and delaying degradation. These interactions of the catalyst at acidic and basic pHs are going to accelerate or retard the degradation rate respectively [29].

-pH2/ TiO_2 -PMMA

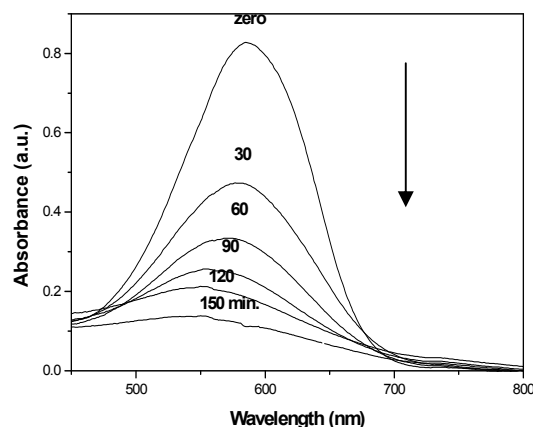


Figure 4: The photobleaching of $1 \times 10^{-5} \text{ mol dm}^{-3}$ TB at $\text{pH}=2$ irradiated in sunlight ($500-600 \text{ W/m}^2$) using 0.08 g TiO_2 -PMMA thin film.

High degradation of trypan blue ($\text{pH}=2$) over 0.08 g TiO_2 -PMMA thin film is given in Figure (4). This behaviour depends on the type of interactions between TB molecules and the catalyst surface. In strong acidic media, interactions between TiOH_2^+ and TB anions are very strong and allow TB to be degraded more easily. Furthermore, for the azo dyes with sulfonic groups in their structures, at low pH range, electrostatic interactions between the positive catalyst surface and dye anions lead to strong adsorption of the dye anions on the metal oxide (TiO_2) support [30,32-33]. Therefore, efficient degradation is due to high electron injection rate from TiO_2 to the adsorbed TB on the surface. From this figure it can be observed that 150 min. sunlight irradiation of TB solution on 0.08 g TiO_2 -PMMA thin film resulted in the decrease of TB up to 87% (table 1) from its initial concentration.

-pH7/ TiO₂-PMMA

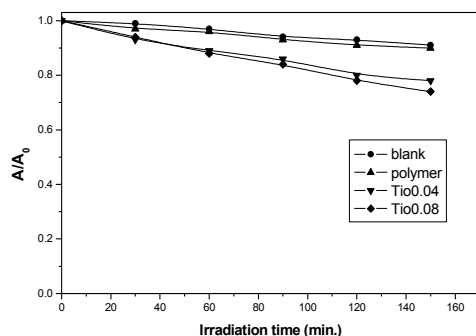


Figure 5: Normalized absorption of TB ($1 \times 10^{-5} \text{ mol dm}^{-3}$, $\lambda_{\text{max}}=585\text{nm}$) against the irradiation time at sunlight irradiance $500\text{-}600 \text{ W/m}^2$ using 0.04 & 0.08g TiO_2 -PMMA at pH7 using optical path length of 1cm .

Figure (5) illustrates similar characteristics in the normalized absorption spectra between the control samples (blank TB and blank TB on PMMA thin film). It also shows no remarkable changes in the normalized curves in cases of 0.04 and 0.08 g TiO_2 . This may be due to that at $\text{pH}=7$, the TiO_2 surface charge is close to zero or slightly negative (i.e no adsorption).[31] Moreover, the molecular complexity of the diazo dye TB reduces the accessibility of the dye molecules to the TiO_2 surface. [3] Consequently, there is no significant difference between 0.04 g and 0.08 g TiO_2 at pH7. Hence the decrease of TB is 25%.

-pH2 Au/TiO₂

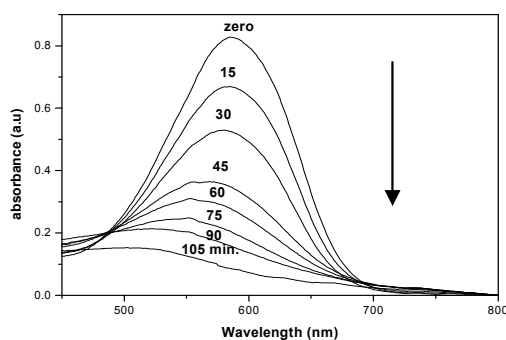


Figure 6: Photobleaching of TB ($1 \times 10^{-5} \text{ mol dm}^{-3}$) at $\text{pH}=2$ irradiated with sunlight ($500\text{-}600 \text{ W/m}^2$) on Au/TiO_2 -PMMA thin film.

The best photodegradation percentage (90%) was taken at $\text{pH}=2$ after 105 minutes using Au/TiO_2 (0.08g)-PMMA thin film as displayed in Figure (6). The deposition of nanosized gold particles on the TiO_2 surface may possibly increase the photocatalytic action of the semiconductor oxide by increasing the efficiency of charge separation of the light-generated electron-hole pairs [35-39]. So the best photocatalytic

activity was attained with Au/TiO_2 -PMMA thin film. This means that actually Au/TiO_2 -PMMA is an effective photocatalyst for the degradation of toxic materials in the wastewater.

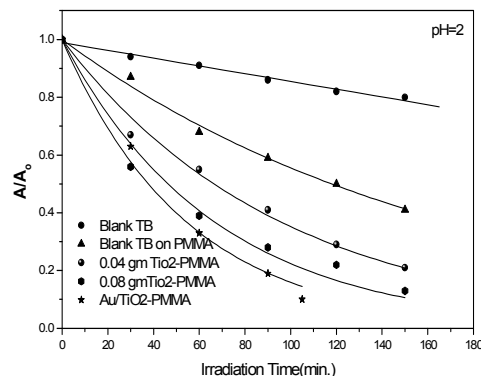


Figure 7: Dependence of photodegradation of TB ($1 \times 10^{-5} \text{ mol dm}^{-3}$, $\lambda_{\text{max}}=585\text{nm}$) on the irradiation time at $\text{pH}=2$ and sunlight irradiance $500\text{-}600 \text{ W/m}^2$ using TiO_2 -PMMA and Au/ TiO_2 PMMA thin films.

Figure (7) confirms that the rate of decomposition assisted by the Au/TiO_2 nanocomposite is faster (105 min.) and more effective than that catalyzed by TiO_2 alone (150 min.) at the same pH value. Table (1) gives the average rate of TB photodegradation. The rate was calculated according to the following equation:

$$\text{Rate} = (A_0 - A_t) / t$$

Where, A_0 is the absorption spectra ($\lambda_{\text{max}}=585 \text{ nm}$) at zero time,

A_t is the absorption spectra ($\lambda_{\text{max}}=585 \text{ nm}$) at a time t . t is the irradiation time in sec. The table illustrates that the rate of photodegradation increases at $\text{pH}=2$ with using Au/TiO_2 (0.08 g). The time required for mineralization in case of TiO_2 (0.08 g) was longer and less efficient than that in case of Au/TiO_2 (0.08 g). This may be due to the presence of gold nanoparticles which decrease the recombination rate between electron-hole pairs and consequently increasing the radicals produced in the medium and enhancing the efficiency of the photodegradation process.

Table 1, gives TB ($1 \times 10^{-5} \text{ mol dm}^{-3}$) photodegradation rate and percentage according to exposure time at $\text{pH}=2$ and $\lambda_{\text{max}}=585\text{nm}$.

Nanoparticle Conc.	Time (min.)	Photodegradation %=($A_0 - A_t$)x100	Photodegradation rate $A_0 - A_t / t$
Blank (0 g)	150	20	$2.2 \times 10^{-5} \text{ mol dm}^{-3} \text{ sec}^{-1}$
TiO_2 (0.04 g)	150	79	$8.8 \times 10^{-5} \text{ mol dm}^{-3} \text{ sec}^{-1}$
TiO_2 (0.08 g)	150	87	$9.7 \times 10^{-5} \text{ mol dm}^{-3} \text{ sec}^{-1}$
Au/TiO_2 (0.08 g)	105	90	$1.4 \times 10^{-4} \text{ mol dm}^{-3} \text{ sec}^{-1}$

Conclusions

Although TB is known for its high photostability. We report a higher TB photodegradation rate using gold deposited on TiO₂ polymer film than using TiO₂ alone at the same pH value. In addition, the photocatalytic degradation was effective in acidic environment, the degradation of TB was at its greatest at acidic pH=2 while it was lowest at basic pH=8.

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